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Vertical Pollution Characteristics of PAHs around an Oil Sludge Storage Site of Jianghan Oil Field of China

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Abstract

A profile of the soil samples around a typical crude oil sludge storage site of Jianghan Oil Field of China were collected and analyzed. We used the UE-GC/FID method to analyze qualitatively and quantitatively the 16 kinds of PAHs which were controlled priory by the U.S.EPA. The results showed that the study area was polluted severely by PAHs. The main pollutants were naphthalene, acenaphthylene, fluorene, phenathrene, chrysene, benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno (1,2,3,-cd) pyrene，dibenzo (a,h) anthracene , benzo (g,h,i) perylene, while the amount of acenaphthene, fluoranthene, pyrene and benzo (a) anthracene was relatively low. The peak values of PAHs in the profiles appeared in the range of 30-40 cm, was 1899 ng·g-1. The ability of different PAHs components to transport downward changed in the profile, which was characterized as 2 rings PAHs>3 rings PAHs>4 rings PAHs>5 rings PAHs>6 rings PAHs.

Keywords: Oil sludge storage site; Soil profile；Contaminated site by crude oil；UE-GC/FID ;PAHs.

Polycyclic aromatic hydrocarbons (PAHs) are a kind of persistent organic pollutants (POPs) which distributed widely in the environment, and had carcinogenic, teratogenic and mutagenic effects on mammalian and human. Some PAHs can react with NO_2, HNO_3, O_3, producing nitro-PAHs and oxidised PAHs of direct mutagenicity. Nitro-PAHs are not only mutagenic, some of which are also carcinogenic. On the 129 "priority pollutants" blacklist which were proposed in 1976 by the U.S. EPA, 16 kinds of them are polycyclic aromatic compounds. PAHs properties of poor water solubility and high octanol - water partition coefficient (Kow) made them easily assigned to living body, soil and sediments. The behaviors of their environmental chemistry are volatilization, photodegradation; absorption, Aging and fixation process in the soil - water medium; and the interaction between plants and microorganisms. The migration path of PAHs in the soil is: pollution source — topsoil — plow bottom layers of the soil — the soil vadose zone underground — underground aquifers [1]. The harm to the human body caused by PAHs into the soil is higher than that of into air and water [2]. Crude oil mining had become the main

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pollutant source of PAHs in soil and groundwater. Large amount of sludge is a wide range of pollutant in oil fields , and in which PAHs are the main factors of POPs. The oil sludge storage site researched located in Jianghan Oil Field of China, with the length of 60 meters and width of 25 meters, where the main pollutants which are harmful to the environment are petroleum hydrocarbons and residues of chemical treatment agent, etc. With the arrival of the rainy season, leakage and contamination can be easily transferred to the surrounding environment and caused great harm. 16 kinds of PAHs in one profile sample collected from the contaminated sites were monitored and analyzed in this paper to provide the basic basis for environmental management and pollution control of this type of contaminated sites.

1. Experimental Reagents and Methods

1.1 Reagents

Anhydrous sodium sulfate (after 600 ℃, 6 h), silica gel (100/200 mesh, 130 ℃, 16 h activation), copper powder with 10% (volume fraction) dilute hydrochloric acid to wash away the impurity metals and metal oxides, and then use distilled water and ultrapure water to wash repeatedly until no significant acid, and then methanol and n-hexane washing. Dichloromethane, acetone, n-pentane, cyclohexane, n-hexane were chromatographic pure. Standard samples were purchased from The Environmental Protection Research Test Institute of Ministry of Agriculture of China.

1.2 Preparation of Standard Solutions

According to GC-FID detection limits and relevant literature, 100 μL mixed standard solution was absorbed accurately and diluted into concentration of C_1 with methanol. Then diluting the C_1 concentration standard solution for 4 times progressively, in order to make the standard sample solution into five concentration gradients: C_1, C_2, C_3, C_4 and C_5.

1.3 Collecting Samples

Samples were collected from 1 m depth profile at the crude oil sludge storage site, and the depth are respectively as: 0-10 cm, 10-20 cm, 20-30 cm, 30-40 cm, 40-50 cm, 50-60 cm, 60-70 cm, 70-80 cm, 80 -90 cm, 90-100 cm. All samples were taken into brown glass bottles, and sealed in the field with the Teflon tape, coldly stored at 4 ℃ to be analyzed later.

1.4 Pretreatment for Soil Samples

Weighted 10g of fresh soil sample, added 20 g of anhydrous sodium sulfate and 0.7g copper powder, grinded and mixed, then added 40 mL, 30 mL, 30 mL of acetone / dichloromethane(1:1，v/v) in sequence. Extracted by ultrasonic extraction(UE) 3 times, each time 20 min, extract liquor was separated by centrifugation (2000 r / min). The supernatant was concentrated by rotary evaporator or nitrogen blow instrument to 1-2 mL, and added 4 mL cyclohexane, concentrated to 2.0 mL again. The concentrated sample was then purified through anhydrous sodium sulfate, silica gel, anhydrous sodium sulfate column (column had been pre-washing by 40 mL pentane, eluent discarded) in sequence, then added 2 mL of cyclohexane to wash and complete the transfer. Eluted chromatographic column with 25 mL pentane, discarded, and then with 50 mL dichloromethane / pentane (2:3, v / v) elution, eluent was collected and concentrated, then got constant volume to 1 mL with hexane to be analyzed later [3-8].

1.5 GC Conditions

Use Agilent6890N Gas Chromatograph; use high pure helium for carrier gas; FID detector; HP-5 (30 m × 0.32 mm × 0.25 μm) chromatographic column; column temperature is from 70 ℃ (to keep 2 min) to 220 ℃ with 15 ℃/min rate, with 2 ℃/min rate rose to 270 ℃, with 5 ℃/min rate rose to 290 ℃ (to keep 3 min); the carrier gas is nitrogen.

2. Results and Analysis

2.1 Vertical Distribution Characteristics of PAHs in Profile

The concentration of PAHs at different depth of the profile showed in Table 1; Vertical distribution of different rings PAHs showed on Fig.1; Vertical distribution of total PAHs showed on Fig.2. Due to 6 rings PAHs are impermeable and insusceptible to oxidation damage, the concentration of 6 rings PAHS were highest at the depth of 0-10 cm, and high rings PAHs were more easily accumulated in the soil surface. However, the concentration of PAHs at the top surface was attenuation because of the photolysis and other acts of migration and transformation (Fig.1). Further down observed that the concentrations of PAHs were varying at different depths in profile: gradually increased from top to the depth of 30-40 cm, where the peak appeared, and then gradually decreased (Fig.2). That's may be soil in this area were dominated by alluvial sandy soil which can play a role of adsorption and enrichment to PAHs. On the other hand, this adsorption and enrichment can retard and retain PAHs downward migration, made them migrate slowly and penetrate down difficultly. However, after many years of long-term pollution there was still a certain amount of PAHs into the soil of 90-100 cm depth because of factors like rainwater leaching and combination with soil clay.

By analyzing the migration of PAHs with different rings in the soil (Table 2 and Fig.1) , we found that the ratio of low molecular weight PAHs (2-3 rings) to total PAHs in surface soils was small, but increased rapidly with the increase of soil depth. The concentration of ∑2 rings PAHs in soil profile depth changed with the peak at 60-70 cm, The concentration of ∑3 rings PAHs in soil profile depth changed with the peak at 40-50 cm, and low rings PAHs higher migration ability; and ∑4 rings PAHs got the peak at 30-40 cm depth, ∑5 rings PAHs got the peak at 30-40 cm depth, then gradually reduced; and 6 rings PAHs with peak at 0-10 cm depth.. Factors affecting the vertical migration of PAHs include the physical and chemical properties of PAHs, content of organic carbon and clay in soil, leaching and human disturbance, etc. 2-3 rings PAHs with the lg K_{OW} <4.9, have higher solubility than high cyclic PAHs, be easy to migrate in solution, while high cyclic

Table 1 Vertical Distribution of PAHs for the Sampling Profile (ng·g-1 dry weight)

No.	PAHs / Depth（cm）		0-10	10-20	20-30	30-40	40-50	50-60	60-70	70-80	80-90	90-100	Holand Limit*
1	Naphthalene	(2) ***	6	9	19	30	31	27	28	27	28	26	15
2	Acenaphthylene	(2)	8	10	12	16	18	54	69	32	21	16	no**
3	Acenaphthene	(2)	—	—	—	—	—	—	—	—	—	—	no
4	Fluorene	(3)	13	15	17	26	29	34	22	16	13	9	no
5	Phenathrene	(3)	11	16	25	33	49	29	25	26	28	25	50
6	Anthracene	(3)	7	6	6	16	7	5	6	4	2	—	50
7	Fluoranthene	(4)	—	—	—	24	8	11	5	8	10	2	15
8	Pyrene	(4)	6	8	11	19	13	3	2	2	3	—	no
9	Benzo(a)anthracene	(4)	—	—	—	—	—	6	11	12	13	8	25
10	Chrysene	(4)	10	18	43	41	10	7	8	6	2	1	20
11	Benzo(b)fluoranthene	(5)	18	19	46	52	18	11	—	—	—	—	no
12	Benzo(k)fluoranthene	(5)	58	43	49	89	56	12	8	7	6	2	25
13	Benzo(a)pyrene	(5)	52	68	78	181	63	59	12	10	5	3	25
14	Indeno(1, 2, 3, -cd)pyrene	(6)	113	109	101	99	92	86	81	12	9	—	25
15	Dibenzo(a,h)anthracene	(5)	742	989	986	981	524	321	89	43	9	6	no
16	Benzo(g, h, i)perylene	(6)	301	298	292	290	221	74	21	9	—	—	20
	ΣPAHs		1345	1608	1689	1899	1130	739	387	214	149	98	

Note： * is soil remediation limit standards established for every PAH by Netherlands; **NO represent unestablished limit standards

***Number is Cycles in Parentheses; —represent less than detection limit.

Table 2 Vertical Distribution of Different Rings PAHs for the Sampling Profile (ng·g-1 dry weight)

Depth (cm) / PAHs	0-10	10-20	20-30	30-40	40-50	50-60	60-70	70-80	80-90	90-100
∑2 cycles	14	19	31	46	49	81	97	59	49	42
∑3 cycles	31	37	48	75	85	68	53	46	43	34
∑4 cycles	16	26	54	84	31	27	26	28	28	11
∑5 cycles	870	1119	1159	1303	661	403	109	60	20	11
∑6 cycles	414	407	393	389	313	160	102	21	9	0

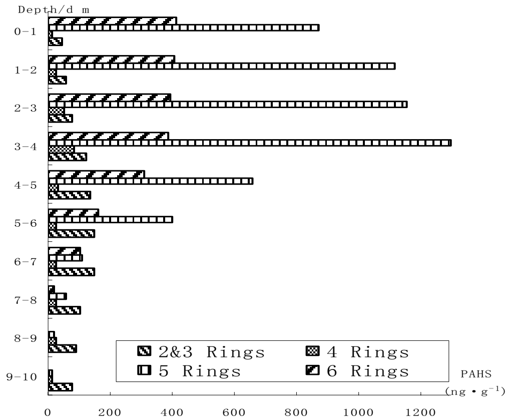

Fig.1 Vertical Distribution of Different Rings PAHs

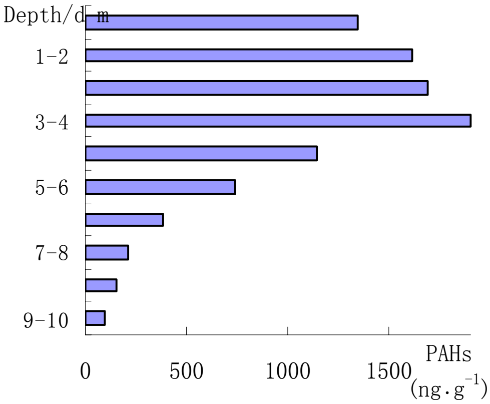

Fig.2 Vertical Distribution of Total PAHs

PAHs mainly migrate in the form of being combined with soil organic matter, which make them difficult to move into the deep soil [11].

2.2 The Total Amount Characteristics of Every PAH in This Profile

The total amount characteristics of every PAH in profile showed in Fig.3. The concentration of the 16 kinds of PAHs which were controlled priory by the USEPA were high, which implied that the surface soil polluted by PAHs in this research area had a negative biological effects. According to the Netherlands soil remediation standards (see Table 2), the mean value of Naphthalene, Benzo(a) yrene, Benzo (g,h,i) perylene and Indeno (1,2,3,-cd) pyrene in profile had exceeded the levels to varying degrees.

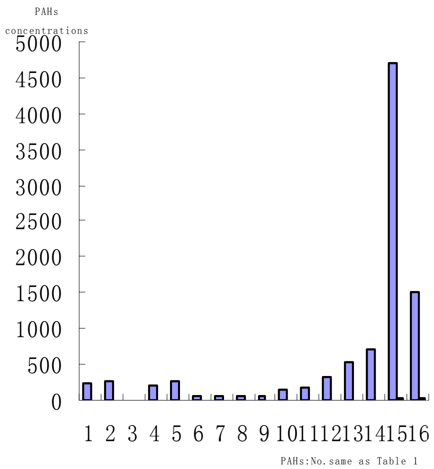

Fig.3 The Total Amount Characteristics of Every PAH in Profile

3. Conclusion

By using the UE-GC/FID method to analyze the concentration and distribution of the 16 kinds of controlled priory PAHs from one profile samples at a typical crude oil sludge storage site, we got the following preliminary conclusions :

The study area was polluted severely by PAHs. The main pollutants were naphthalene, acenaphthylene, fluorene, phenathrene, chrysene, benzo(b)fluoranthene, benzo(k) fluoranthene, benzo (a) pyrene, indeno (1,2,3,-cd) pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, while the amount of acenaphthene and benzo(h)anthracene was relatively low. The peak values of PAHs in the profiles appeared in the range of 30-40 cm was 1899 $ng \cdot g^{-1}$.

The correlation between the distribution of PAHs in surface and subsurface and their own physical and chemical properties is high. 2-3 rings PAHs showed a strong ability to migrate downward. In surface soil, 2-3 rings PAHs accounted for a fraction of the overall content of PAHs, but the proportion increased rapidly with the deepening of the soil profile. High cyclic PAHs are mostly enriched in the soil surface. The ability of different PAHs components to transport downward changed in profile, which was characterized as 2 rings PAHs>3 rings PAHs>4 rings PAHs>5-6 rings PAHs.

The highest concentration of PAHs in profile appeared at the depth of 30-40 cm. PAHs at the depth of 90-100 cm soil layer is also detected, indicating that the downward migration of PAHs had contaminated the deep soil. Considerings of local higher water table, and with the advent of the rainy season, groundwater could be easily polluted, which should be taken seriously.

4. Acknowledgment

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References

[1] D P Xu. A study on distribution characteristics of typical petroleum hydrocarbons in different kinds of environmental media. pp.5, 2005.

[2] C A Menzie, B B Potocki, J Santodonato. Exposure to carcinogenic PAHs in the environment, vol.26, no.7, pp.1278,1992.

[3] EPA．Method 8100-Polynuclear Aromatic Hydrocarbons GC, EPA SW-846 On-line 8000 Series Methods, pp.3,1986.

[4] EPA. Method 3550b-Ultrasonic Extraction, EPA SW-846 On-line 3000 Series Methods, pp.1,1996.

[5] EPA．Method 3630c-Silica Gel Cleanup,EPA SW-846 On-line 3000 Series Methods, pp.1,1996.

[6] R Xiao, Q H Wang, X M Du, et al. Vertical distribution characteristics of polycyclic aromatic hydrocarbon in typical wastewater irrigated soils, vol.19, no.6, pp.49, 2006.

[7] Y J Zhang, S Q Zhu, R Xiao, ea al. Study on distribution of PAHs in groundwater in irrigation area along the Hunhe river in Liaoning province, vol.20, no.1, pp.7, 2007.

[8] L L Ma, W J Lao, X T Wang, ea al. Analytical method for trace semi-volatile organic compounds in the soil of Beijing suburbs, vol.31, no.9, pp.1025, 2003.

[9] E R Long, D D MacDonald, S L Smith, ea al. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, no.19, pp.81, 1995.

[10] G J Aannokkee. MT-TNO research into the biodegradation of soils and sediments contaminated with oils and PAHs．In：Wolf K (ed.) Contaminated Soil, 1990.

[11] J Chen, X J Wang, S Tao. The influences of soil total organic carbon and clay contents on PAHs vertical distributions in soils in Tianjin area, vol.18, no.4, pp.79, 2005